124

QUALITY CONTROL DATA REPORT FOR THE LIMNOLOGY SECTION DORSET RESEARCH CENTRE

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QUALITY CONTROL DATA FOR THE LIMNOLOGY SECTION DORSET RESEARCH CENTRE

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PREFACE

The Data Report Series is intended as a readily available source of basic data collected for lakes and watersheds in Ontario. These data were collected as part of the Lakeshore Capacity Study and/or the Acid Precipitation in Ontario Study.

The limnological portion of the Lakeshore Capacity Study (1975-81) was initiated to investigate the relationships between lakeshore development and lake trophic status in low ionic strength Precambrian lakes. The Acid Precipitation in Ontario Study (1979-present) was initiated, in part, to investigate the effects of the deposition of strong acids on aquatic and terrestrial ecosystems in Ontario. The primary findings of these studies have been and will continue to be published as reviewed papers and technical reports.

ABSTRACT

This report describes the Quality Control programme at the Dorset Research Centre as part of the environmental studies being carried out by the Limnology Section of the Ministry of the Environment. The Quality Assurance Management programme was presented in an earlier report (Locke, 1985).

A major part of this project is the documentation of analytical methodologies and comparative sampling studies. Many of the study results are presented in this report. This documentation process is an on-going one and will continue as it has in the past, as new projects and studies are developed.

A comprehensive quality control study was undertaken in 1983 to evaluate the contribution of the sample collection and the analytical procedures to the variation in the reported precision of each chemical parameter measured. Certain parameters were identified to be outside the range of acceptable precision criteria as reported by the Laboratory Services Branch of the Ministry of the Environment.

Locke, B.A. 1990. Quality Control Data Report for the Limnology Section, Dorset Research Centre. Ont. Min. Environ. Data Report DR 90/3.

RÉSUMÉ

Ce rapport décrit le Programme de contrôle de la qualité du Centre de recherches de Dorset faisant partie des études environnementales effectuées par la Section de limnologie du ministère de l'Environnement. Le Programme de gestion de l'assurance de la qualité a été présenté dans un rapport antérieur (Locke, 1985).

La documentation des méthodologies analytiques et des études d'échantillonnage comparatives constitue une partie importante de ce projet. Plusieurs résultats de cette étude sont présentés dans ce rapport. Ce processus de documentation est en cours et se poursuivra, tel que par le passé, lorsque de nouveaux projets et études seront développés.

Une étude détaillée du contrôle de la qualité a été entreprise en 1983 pour évaluer la contribution des méthodes d'échantillonnage et des méthodes analytiques à la variation dans la précision rapportée de chacun des paramètres chimiques mesurés. Certains paramètres ont été identifiés comme étant à l'extérieur des limites des critères de précision acceptables, tel que rapportés par la Direction des services de laboratoire du ministère de l'Environnement.

TABLE OF CONTENTS

				Page
PREFACE				i
ABSTRACT				ii
1.	INTRODUCTION			1
2.	QUALITY CONTROL MANAGEMENT			2
	2.1	Scope		2
	2.2	Intercomparison Study Results		2
		2.2.1	Sample Site Location	2
			2.2.1.1 Lake Outflow Sampling Sites	3
			2.2.1.2 Precipitation Sampling Sites	11
		2.2.2	Analytical Technique	12
			2.2.2.1 Sulphate Analytical Methodology	13
			2.2.2.2 Chlorophyll Analytical Methodology	14
			2.2.2.3 Estimation of Colour	20
			2.2.2.4 Trace Metal Analytical Methodology	24
		2.2.3	Collection Methods	25
			2.2.3.1 Precipitation Sample Collection (DRC)	25
			2.2.3.2 Precipitation Sample Comparison Between DRC and ARB	28
			2.2.3.3 Precipitation Depth Estimates	31
			2.2.3.4 Streams Dissolved Oxygen Sample Collection	34
			2.2.3.5 Hydrology - Measurement of Stream Flow	35
			2.2.3.6 Lakes - Estimation of the Euphotic Zone	37
			2.2.3.7 Phytoplankton Collection Methods	40
			2.2.3.8 Lake Water Sample Collection Methods	40
			2.2.3.9 Lake Temperature Profile Measurements	41

2.2.3.10 Zooplankton Collection Methodology 43
2.2.3.11 Sample Container Evaluations 44

3. QUALITY CONTROL REPLICATE PROGRAMME 1983-1987 45
3.1 Experimental Procedures 45
3.2 Statistical Results and Evaluation 46
3.3 Long-term Trend Evaluation 55
3.4 Recommendations/Future Plans 56

4. DATA MANAGEMENT 57
4.1 Scope 57
4.2 Data Base Storage 57
4.3 Data Evaluation 60

5. QUALITY ASSURANCE MANAGEMENT PROGRAMME 61

6. QA/QC EVALUATION AND RECOMMENDATIONS 62

7. REFERENCES 63

8. APPENDICES 67

8.1 Abbreviations used for chemical parameters cited in this report. 67

8.2 Quality control replicate chemistry data range summary by parameter by lake strata. 68

8.3 Stream sample type QC chemistry data summary by parameter. 69

8.4 Precipitation sample type QC chemistry data summary by parameter. 70

LIST OF TABLES

		Page
Table 2.1	Linear regression comparison of outflow sites upstream (at lake) and downstream (at control structure) for five study lakes.	4
Table 2.2	Summary of the results of signed ranks and hypothesized difference of the variance between the sites upstream (at lake) and downstream (at control structure) for Chub, Crosson, Plastic, Red Chalk and Heney outflows.	7
Table 2.3	Summary of linear regression comparison of precipitation chemistry for two concurrently monitored precipitation sites near Heney and Plastic Lakes. The new sites are located less than 0.5 km from the old sites.	10
Table 2.4	Linear regression comparison between SO_4 analysed by IC (dependent) and SO_4 by MTB (independent) based on various selection criteria. All SO_4 analysis reported units in mg/L.	15
Table 2.5	Stepwise regression comparison of SO_4 by IC (dependent) and SO_4 by MTB, automated COLTR, Klett-Summerson COLTR and DOC, (independent variables to enter) for DRC water samples.	16
Table 2.6	Linear regression comparison of cellulose nitrate membrane filters and nylon filters used in the analysis of chlorophyll, (as reported by the DRC and the LSB)	19

Table 2.7 Linear regression comparison of three colour estimation procedures (COLAP, COLTR (1.35) and COLTR (1.65) measured on water chemistry samples at the field lab in Dorset, October 1984. 22

Table 2.8 Linear regression comparison of the Dorset lab and the Inorganic Trace Contaminent lab (ITC) analysis of total zinc (ZNUT) and aluminum (ALUT), 1983 data. The Dorset data was the dependent variable in the regression analysis in all comparisons. 26

Table 2.9 Linear regression comparison of the Dorset lab and the Inorganic Trace Contaminant lab (ITC) lab for ZNUT, PBUT and CDUT (AAS and ASV), 1985-1987 data. The Dorset lab data is the dependent variable in all comparisons. 27

Table 2.10 Linear regression comparison of two bulk precipitation collectors at the Paint Lake site. 29

Table 2.11 Linear regression comparison of the precipitation sample volume (dependent variable) versus the precipitation gauge depth as an estimate of precipitation amount. 33

Table 2.12 Line regression comparison of the estimation of the euphotic zone by the Secchi disc (independent) and a light profile using a Li-192 cosine-corrected quantum sensor (dependent). 39

Table 2.13 Linear regression comparison of tube composite water samples (dependent) and epilimnion volume-weighted water samples. 42

Table 3.1 Quality control replicate statistics of water chemistry samples for study lakes, streams and precipitation sampling sites at the Dorset Research Centre, 1983-1987. 48

Table 3.2 Chemical parameters replicated in the Quality Control Replicate program at Dorset that exceed Lab Services Branch (LSB) reported precision criteria. 54

1. INTRODUCTION

The quality assurance management programme of the Limnology Unit of the Dorset Research Centre was outlined by an earlier report, Locke (1985). That report described the goals, organization and responsibility of the research studies. The experimental procedures involved in the quality control sampling were also described.

The basis for any scientific study is to collect and report data which are complete, accurate, precise and representative. A quality assurance programme must isolate and quantify any or all sources of error or procedure variation. The sources of variability in the data base have been assessed by the collection and analysis of special quality control (QC) samples. The details of this QC sampling methodology and the evaluation of sampling intercomparisons are presented in this report.

2. QUALITY CONTROL MANAGEMENT

2.1 Scope

The quality of our data are monitored on a routine basis. This involves the continual assessment of all aspects of the data collection process, and is not limited to analytical procedures. Comparison between different sampling and analytical techniques provides the basis for preliminary evaluation. Specific statistical procedures will define the relationship of the comparison. The results of many of these intercomparison studies are presented in the following sections. They are categorized according to the component of the data collection process being investigated.

2.2 Intercomparison Study Results

2.2.1 Sample Site Location

The location of the sampling site must meet acceptable siting criteria such that it is representative of naturally occurring conditions. Many sampling sites have been evaluated to estimate any biases one site may have over the other. The results of each of these comparisons are summarized as follows:

2.2.1.1 Lake Outflow Sampling Sites

A comparison study was done in 1980 to test for chemical differences in outflow chemistry based on the location of the sampling site. Chemical samples are routinely taken at the control structure of the stream. The outflow chemistry should be comparable to the concentrations found in the water in the lake itself, at or near the point where the outflow exits from the lake. Many of our study lakes however, have control structures at a considerable distance downstream from the lake, (several are 50 m or more from the lake shoreline). This distance, coupled with any 'ponding' effect on the outflow water, (especially during periods of low flow), might substantially affect the chemistry.

Five lake outflows were selected with control structures separated from the lake by ponds or low-lying terraine. Sampling sites were established at Chub, Plastic, Crosson and Red Chalk lakes at a spot as close to the lake as possible. A similar comparison was made at the Heney Lake outflow in 1985. Table 2.1 summarizes the linear regression results for all five sites.

Chub, Crosson, Plastic, and Red Chalk were sampled during the period of January 1980 to March 1981. Heney Lake was sampled during the period of October 1984 to January 1986. The upstream (lake) sample was regressed as the dependent variable in all comparisons.

Table 2.1. Linear regression comparison of outflow sites upstream (at lake) and downstream (at control structure) for five study lakes.

Outflow Parameter*	N	r	intercept	slope	95% CI about slope lower	95% CI about slope upper	Means up (lake)	Means down (control)
CHUB								
PPUT	16	0.494	-0.178	1.182	-0.012	2.376	9.95	8.57
NNOTFR	13	0.939	2.388	0.859	0.651	1.069	50.00	55.38
NNHTFR	13	0.958	1.279	0.866	0.694	1.038	35.77	39.85
NNTKUR	13	0.392	-25.322	1.238	-0.692	3.168	372.69	321.54
pH	17	0.978	0.282	0.938	0.828	1.048	5.44	5.50
COLAP, COLTR*	16	0.836	7.740	0.892	0.557	1.226	38.00	33.94
COND	16	0.794	15.683	0.449	0.252	0.646	28.75	29.13
ALKTI	15	0.946	-0.078	0.975	0.775	1.175	0.33	0.41
ALKT	15	0.966	-0.015	1.037	0.870	1.204	2.19	2.25
CROSSON								
PPUT	17	0.841	-0.161	0.984	0.637	1.332	8.45	8.74
NNTKUR	14	0.007	345.6	0.008	-0.715	0.731	348.21	316.88
pH	17	0.884	-0.110	1.017	0.722	1.312	5.71	5.72
COND	17	0.718	2.038	0.910	0.425	1.395	26.18	26.53
ALKTI	16	0.539	0.251	0.509	0.053	0.965	0.48	0.47
ALKT	16	0.920	-0.010	1.001	0.756	1.246	2.23	2.23
NNOTFR	11	0.998	0.308	0.983	0.941	1.024	43.18	52.50
NNHTFR	11	0.936	-0.489	0.949	0.680	1.217	25.73	27.64
PLASTIC								
PPUT	19	0.582	3.652	0.722	0.205	1.238	9.13	7.48
NNTKUR	17	0.503	101.688	0.733	0.039	1.427	314.12	289.71
pH	20	0.726	2.350	0.573	0.304	0.841	5.62	5.72
COLAP, COLTR	20	0.579	3.625	0.608	0.184	1.033	9.10	9.00
COND	20	0.642	12.378	0.503	0.205	0.800	25.55	26.20
ALKTI	17	0.657	0.304	0.311	0.115	0.508	0.66	0.98
ALKT	17	0.681	1.283	0.402	0.164	0.640	2.41	2.69
NNOTFR	13	0.694	3.367	0.546	0.170	0.922	27.31	43.85
NNHTFR	13	0.993	2.766	1.115	1.026	1.205	60.08	51.38

Table 2.1. (Cont'd)

Outflow Parameter*	N	r	intercept	slope	95% CI about slope lower	95% CI about slope upper	Means up (lake)	Means down (control)
RED CHALK								
NNOTFR	12	0.987	-1.902	1.020	0.904	1.137	72.50	72.92
NNHTFR	12	0.956	0.545	1.211	0.951	1.471	32.33	26.25
NNTKUR	17	0.710	55.512	0.799	0.363	1.235	255.00	249.71
pH	19	0.908	-2.673	1.417	1.082	1.751	6.34	6.37
COLAP, COLTR	19	0.882	2.217	0.829	0.612	1.056	9.89	9.26
COND	19	0.778	4.307	0.853	0.500	1.206	29.89	30.00
ALKTI	17	0.866	-0.501	1.127	0.769	1.485	2.86	2.98
ALKT	17	0.915	1.478	1.294	0.980	1.607	4.63	4.72
HENEY***								
ALKT	70	0.804	0.255	0.765	0.628	0.901	1.82	2.23
ALKTI	69	0.809	-0.134	0.733	0.604	0.864	0.08	0.60
ALUT	71	0.874	-4.372	0.966	0.838	1.096	74.79	83.52
CAUR	72	0.679	0.624	0.649	0.482	0.816	2.02	2.26
CLIDUR	71	0.225	0.502	0.173	-0.007	0.353	0.63	0.86
COLTR	73	0.720	5.250	0.597	0.461	0.733	13.18	13.68
COND	72	0.767	2.289	0.884	0.707	1.061	27.24	29.63
DIC	73	0.451	0.428	0.528	0.281	0.776	1.37	1.67
DOC	71	0.812	0.678	0.790	0.653	0.927	2.91	3.12
FEUT	72	0.823	74.133	0.210	0.176	0.245	108.89	163.38
FFIDUR	73	0.836	-2.558	1.055	0.891	1.219	45.26	45.31
KKUR	69	0.784	0.205	0.502	0.405	0.599	0.45	0.47
MGUR	71	0.802	0.079	0.811	0.666	0.956	0.53	0.58
MNUT	67	0.835	10.115	0.763	0.639	0.887	41.44	52.49
NAUR	71	0.345	0.469	0.251	0.087	0.415	0.65	0.78
NNHTFR	71	0.989	-1.476	1.204	1.062	1.345	34.07	35.53
NNOTFR	68	0.933	-42.282	1.005	0.909	1.099	100.18	166.67
NNTKUR	70	0.704	63.552	0.810	0.613	1.008	250.68	250.69
pH	72	0.921	-0.706	1.133	1.019	1.247	5.30	5.31
PPUT	57	0.615	3.283	0.541	0.353	0.728	6.91	9.82
SIO3UR	71	0.888	-0.125	1.053	0.921	1.184	0.58	0.72
SS04UR	71	0.838	0.617	0.914	0.771	1.056	7.23	7.09

* Units are given in Appendix 8.1.

** COLAP and COLTR were measured in 1980 (results are for both methods).

*** 2-3 summer 1985 points removed from downstream data set due to extreme contamination/concentration ... symptomatic of the problem being investigated.

The linear regression summary shows that both PPUT and NNTKUR are significantly different between the two sampling stations for all 5 sites. NNTKUR and PPUT are done on the same unfiltered sample digest. Much of the variation could be due to differences in suspended matter. The sampling stations at Heney, Chub and Plastic outflows also show marked differences in many other parameters. The comparisons at Red Chalk and Crosson outflow are not so conclusive. Other than NNOTFR, NNHTFR and NNTKUR, the two sampling sites at Crosson and Red Chalk compare well considering the small sample size. In most cases though, the chemistry downstream at the control structure had higher measured values. This fact alone would suggest some influence due to the distance between the lake proper and the regular sampling site. Since some parameters change very little with time, a non-significant correlation can result even though the results are equivalent within the limits of our analytical capabilities. We therefore compared the data pairwise using the Wilcoxon-Signed Rank test and a paired sample test for variance.

Table 2.2 summarizes the results of the paired tests. The signed rank and hypothesized difference in the variance is demonstrated by the significance of the probability value. These two tests however cannot estimate the magnitude of any significant difference. The Wilcoxon-signed ranks tests the differences between each data pair. The null hypothesis is that the frequency distribution of the measurements is the same for the upstream and downstream members of a pair. This result of this null hypothesis is that each rank is equally likely to be positive or

Table 2.2. Summary of the results of signed ranks and hypothesized difference of the variance between the sites upstream (at lake) and downstream (at control structure) for Chub, Crosson, Plastic, Red Chalk and Heney outflows.

Outflow / Parameter**	N	Prob (2-tail) signed rank Ho:med(lake) = med(control)	Ho:Var (lake) = Var(control) F stat	P value
CHUB				
PPUT	16	0.25599	* 5.736	0.00082
NNOTFR	13	0.10881	1.193	0.38241
NNHTFR	13	0.06188	1.225	0.36549
NNTKUR	13	0.30782	* 9.989	0.00018
pH	17	* 0.00081	1.088	0.43404
COLAP/COLTR	16	0.15513	1.136	0.40393
COND	16	0.28505	* 3.131	0.01702
ALTI	15	* 0.00451	1.062	0.45573
ALKT	15	0.09384	1.154	0.39615
CROSSON				
PPUT	17	0.25591	1.369	0.26871
NNTKUR	14	0.80173	1.022	0.47874
pH	17	0.50145	1.322	0.29131
COLAP/COLTR	16	0.30656	1.145	0.39665
COND	17	0.17630	1.605	0.17698
ALKTI	16	0.91763	1.296	0.31043
ALKT	16	0.62326	1.184	0.37363
NNOTFR	11	0.59298	1.384	0.30801
NNHTFR	11	0.59371	1.027	0.48378
PLASTIC				
PPUT	19	* 0.01259	1.595	0.16059
NNTKUR	17	0.12515	2.127	0.07087
pH	20	* 0.03656	1.608	0.15453
COLAP/COLTR	20	0.62407	1.104	0.41550
COND	20	0.10264	1.628	0.14828
ALKTI	17	* 0.01794	* 4.422	0.00188
ALKT	17	* 0.01997	* 2.901	0.01717
NNOTFR	13	* 0.03569	1.616	0.20871
NNHTFR	13	* 0.00287	1.262	0.34659

Table 2.2. (Cont'd)

Outflow		Prob (2-tail) signed rank Ho:med(lake) = med(control)	Ho:Var (lake) = Var(control)	
Parameter**	N		F stat	P value
RED CHALK				
NNOTFR	12	0.86577	1.068	0.45724
NNHTFR	12	* 0.04545	1.603	0.22320
NNTKUR	17	0.33876	1.267	0.32096
pH	19	0.79386	* 2.434	0.03345
COLAP/COLTR	19	0.44687	1.132	0.39792
COND	19	0.77943	1.203	0.34974
ALKTI	17	0.11278	1.694	0.15113
ALKT	17	0.26595	1.997	0.08862
HENEY				
ALKT	73	* 0.00000	* 7.523	0.00000
ALKTI	73	* 0.00000	* 11.940	0.00000
ALUT	72	* 0.00195	1.090	0.35892
CAUR	74	* 0.00000	* 9.005	0.00000
CLIDUR	73	* 0.00000	* 47.254	0.00000
COLTR	74	0.67123	* 2.059	0.00118
COND	74	* 0.00000	* 7.900	0.00000
DIC	74	* 0.04780	* 1.900	0.00336
DOC	72	* 0.03555	* 27.530	0.00000
FEUT	72	0.50788	* 14.943	0.00000
FFIDUR	73	0.88157	* 1.593	0.02495
KKUR	73	* 0.03835	* 2.399	0.00013
MGUR	73	* 0.00000	* 7.777	0.00000
MNUT	71	0.23652	* 21.266	0.00000
NAUR	73	* 0.00000	* 24.270	0.00000
NNHTFR	73	* 0.00233	* 1.777	0.00787
NNOTFR	73	* 0.00000	* 1.609	0.02268
NNTKUR	72	* 0.00141	* 5.869	0.00000
pH	73	0.73100	1.114	0.32274
PPUT	60	0.83262	* 56.598	0.00000
SI03UR	73	* 0.00000	1.251	0.17135
SS04UR	73	0.92923	* 4.512	0.00000

* Denotes a significant difference at the .05 level of significance
Note: in all cases the lake (upstream) value was subtracted from the control, (downstream) value to obtain the ranked differences.

** Units are given in Appendix 8.1.

negative. A large difference between the two sign ranks, (or paired differences), does not show size of difference between the two sites but rather than one of the sites has uniformly higher, (or lower) values than the other one. The results shows that many parameters are significantly different between the two sampling sites at Chub, Plastic and Heney. Red chalk shows only NNHTFR significantly different and Crosson shows no significant results.

An hypothesis test for the equality or inequality of the variances show that Chub, Plastic and Heney have between-site differences. Crosson again shows no significant differences and Red Chalk variance in pH is significantly different between the up and down stream sites.

To summarize, both Chub and Plastic Lake outflow sampling sites are presently located at stations downstream for the lake proper. There is not enough statistical evidence to suggest that the sampling sites at Red Chalk and Crosson outflows should be moved upstream from their present location. The results from Heney Lake show conclusively that there are very significant differences between the up and downstream sampling sites. The Heney outflow sampling site was moved closer to the lake in July 1986.

Table 2.3 Linear regression comparison of precipitation chemistry for two concurrently monitored precipitation sites near Heney and Plastic Lakes. The new sites are located less than 0.5 km from the old sites.

Site / Parameter*	N	r	intercept	slope	95% CI about slope lower	95% CI about slope upper	Site Means New	Site Means Old
HENEY								
depth	27	0.930	0.470	0.957	0.802	1.112	21.37	21.80
ALKTI	26	0.876	-0.664	0.905	0.695	1.116	-2.74	-2.69
ALUT	27	0.968	1.087	1.262	1.129	1.396	34.85	26.74
CAUR	27	0.995	-0.020	1.080	1.037	1.138	0.43	1.42
CLIDUR	27	0.942	-0.007	0.987	0.843	1.132	0.15	0.16
COND	27	0.969	0.581	1.041	0.932	1.151	34.71	32.78
DOC	27	0.961	0.050	0.937	0.827	1.047	0.96	0.97
FEUT	27	0.611	**45.55	1.205	0.562	1.848	85.85	33.44
FFIDUR	27	0.984	0.164	10.69	0.989	1.149	7.16	6.54
KKUR	27	0.932	-0.012	0.800	0.672	0.929	0.13	0.17
MGUR	27	0.990	-0.008	1.070	1.009	1.131	0.08	0.08
MNUT	27	0.937	-1.302	1.240	10.49	1.430	7.93	7.44
NAUR	27	0.811	0.010	0.859	0.604	1.115	0.06	0.06
NNHTFR	26	0.863	80.668	0.730	0.549	0.910	451.00	523.19
NNOTFR	27	0.967	-33.66	1.082	0.965	1.199	520.74	512.41
NNTKUR	11	0.991	17.845	0.894	0.803	0.985	564.09	610.91
pH	25	0.938	0.096	0.968	0.814	1.122	4.32	4.38
PPUT	23	0.922	-11.257	0.906	0.733	1.079	43.38	62.86
SI03UR	27	0.587	0.008	0.475	0.205	0.745	0.02	0.02
SS04UR	27	0.986	0.184	0.981	0.914	1.049	3.76	3.87
PLASTIC								
depth	23	0.976	0.946	0.856	0.858	1.053	19.85	19.78
ALKTI	21	0.957	-0.685	0.801	0.685	0.917	-3.43	-2.72
AKUT	23	0.792	9.383	0.994	0.646	1.340	34.78	25.57
CAUR	23	0.929	-0.027	0.819	0.670	0.967	0.31	0.41
CLIDUR	23	0.868	-0.012	1.232	0.911	1.553	0.15	0.13
COND	23	0.989	1.639	0.957	0.891	1.023	33.33	33.10
DOC	23	0.925	0.105	0.927	0.754	1.100	0.88	0.84
FEUT	22	0.855	10.947	1.029	0.738	1.321	49.55	36.52
FFIDUR	23	0.970	0.969	0.984	0.792	0.995	6.69	6.40
KKUR	23	0.769	0.035	0.664	0.414	0.914	0.09	0.09
MGUR	23	0.782	0.004	0.547	0.349	0.745	0.05	0.09
MNUT	22	0.970	3.167	0.514	0.454	0.574	7.05	7.48
NAUR	23	0.625	0.026	0.863	0.373	1.353	0.07	0.05
NNHTFR	23	0.991	2.028	0.988	0.928	1.047	378.65	381.26
NNOTFR	23	0.992	-2.849	0.970	0.913	1.027	483.26	501.09
NNTKUR	12	0.936	28.041	1.003	0.736	1.269	450.42	421.25
pH	23	0.937	0.744	0.821	0.682	0.959	4.32	4.35
PPUT	21	0.971	2.449	0.915	0.806	1.024	28.88	28.90
SI03UR	22	0.742	0.007	0.431	0.249	0.612	0.02	0.02
SS04UR	23	0.996	0.177	0.934	0.896	0.972	3.47	3.53

* Units are given in Appendix 8.1.

** Some outliers present in new site data ... left in comparison.

2.2.1.2 Precipitation Sampling Sites

In March 1984, 3 of the 4 DRC monitored precipitation collection sites were moved a short distance to new locations. Two of the three sites, (Heney and Plastic) were monitored at the old site as well, to test any possible differences at the new location. Duplicate sampling continued from March 1984 to November 1984. Table 2.3 shows the results of linear regressions between the data collected at the new site and the old site. The new site is treated as the dependent variable in all cases.

The linear regressions results show good comparisons for most chemical parameters measured. There were a few outliers in the comparison data base; left in as noted. The new sites at Heney and Plastic were in more open field conditions, and less influenced by surrounding forest cover. Some of the differences noted between the two sites were for parameters most affected by tree canopy (PPUT, NNOTFR, NNHTFR, NNTKUR, ALUT). Values measured at the old site were higher for these parameters. Some of the other poor regressions, (SI03UR and NAUR), are probably due to the small range of measured values in the comparison data set. Based on this comparison, the monitoring of the old sites for these two stations was discontinued in November of 1984.

2.2.2 Analytical Technique

A quality assurance problem arises when analytical techniques are changed or altered midway through a study. These changes often improve the accuracy and precision of the reported data. If there is a significant difference between the two techniques, a continuous data record is lost. The new analytical procedure could be discontinued in favour of the old one. This option, however, negates the data are proved to be more accurate and precise with the new technique. The second option is to 'convert' either the old or new data using some calculated conversion factor. The option where conversions are applied to the data, often in series, may result in each step deriving in a poorer estimate. If the new technique is more accurate and a sound conversion factor has been derived, previously measured results may be corrected. A conversion factor may be dependent on several interacting spacial and temporal factors, and thus difficult to determine. Conversion factors can be calculated through stepwise or linear regression analysis. The Lab Services Branch (LSB) and the field lab (Dorset Research Centre -DRC) take replicate measurements of any proposed analytical procedures with current techniques. The field lab comparison is very important to test real sampling conditions and associated data variance. This section presents several data sets and summarizes the results of the comparisons.

2.2.2.1 Sulphate Analytical Methodology

On June 23, 1980, the LSB revised the procedure for the analysis of sulphate (SO_4). The method was changed from colourimetric using methylthymol blue (MTB) to automated suppressed ion chromatography (IC).

Analytical results showed a significant decrease using the ion chromatography method. The LSB analysed stream and precipitation samples by both techniques prior to the method change. Their results show only precipitation samples correlated well, (Crowther and Wright, 1980 and Crowther and McBride, 1981). Precipitation samples have low colour, and do not influence MTB analysis. Samples with higher colour however, greatly affect analysis by MTB since the method is colorimetric in nature.

From February to August 1985, approximately 1450 duplicate (lake, stream and precipitation) samples were analyzed by both the MTB and IC SO_4 methods. A new automated colour analytical method, the existing Klett-Summerson colour (COLTR) analysis and DOC were also measured for this same data base for comparison with SO_4. The comparative data base included precipitation samples with low SO_4 and colour levels and stream and lake samples with a full range of SO_4 and colour. Table 2.4 summarizes the liner regression results between the two SO_4 methods, showing different comparison criteria. The LSB regression results for streams are from

Crowther and Wright, 1980 and precipitation sites are from Crowther 1981. Table 2.5 shows the results of stepwise regression analysis with MTB SO_4, COLTR and DOC. SO_4 by IC was regressed as the dependent variable in all comparisons.

Samples with high colour do not show good comparison between the two SO_4 methods. Further comparison on these samples was made on a site by site basis. An accurate conversion factor could not be derived for many stream sites due to temporal variation for both SO_4 and colour. Currently, any SO_4 measured by MTB (pre June 23, 1980) are not used in any data modelling or trend analysis.

2.2.2.2 **Chlorophyll Analytical Methodology**

Chlorophyll is determined by a spectrophotometric method. The field lab filters the samples and ships them covered and frozen to the Toronto Water Quality Lab for analysis. In 1985, the LSB released a report outlining a proposed modification to the analysis, (Crowther and Bobar, 1985).

The filters used at the field lab from 1976 to 1985 were 1.2 μ cellulose nitrate membrane filters. These filters were to be replaced by nylon filters, (available in the same pore size, and suitable for chlorophyll analysis). The nylon filters

Table 2.4 Linear regression comparison between SO_4 analysed by IC (dependent) and SO_4 by MTB (independent) based on various selection criteria. All SO_4 analysis reported units in mg/L.

data selection criteria	N	r	intercept	slope	95% CI about the slope	
All samples	1438	0.446	2.615	0.419	0.374	0.460
All lakes (excl. Sudbury)	192	0.180	5.466	0.150	0.033	0.267
Preciptation sites:						
DRC comparison study	38	0.819	0.312	0.954	0.728	1.179
LSB comparison study	218	0.968	0.192	0.997	-	-
Streams:						
all sites	984	0.302	3.069	0.334	0.268	0.400
LSB comparison study	19	0.705	2.576	0.899	-	-
colour < 30	191	0.724	2.619	0.586	0.506	0.667
colour < 100	648	0.757	1.416	0.649	0.606	0.69
colour > 100	331	0.374	0.554	0.335	0.245	0.425
All samples:						
colour < 30	440	0.925	1.444	0.729	0.701	0.757
colour < 100	1036	0.830	1.520	0.654	0.627	0.681
colour > 100	371	0.385	0.561	0.351	0.260	0.433
All samples:						
DOC < 5	632	0.903	1.282	0.727	0.700	0.754
DOC > 25	79	0.309	-0.112	0.173	0.052	0.294
Streams:						
DOC < 5	310	0.765	1.622	0.684	0.619	0.748
DOC < 10	667	0.767	1.114	0.679	0.635	0.722
DOC < 25	901	0.652	-0.145	0.729	0.674	0.785
DOC > 25	76	0.316	-0.314	0.187	0.057	0.316

Table 2.5 Stepwise regression comparison of SO_4 by IC (dependent) and SO_4 by MTB, automated COLTR, Klett-Summerson COLTR and DOC, (independent variables to enter) for DRC water samples.

data selection criteria	variables	step	N	r	intercept	slope
all samples	ks COLTR	1	1394	0.641	7.830	-0.015
	MTB SO_4	2		0.935	1.723	0.722
	DOC	3		0.938	1.742	-0.080
(ks COL < 30)	MTB SO_4	1	440	0.925	1.444	0.729
	ks COLTR	2		0.931	1.804	-0.028
(ks COL < 100)	MTB SO_4	1	1036	0.830	1.521	0.654
	ks COLTR	2		0.898	1.800	-0.026
(ks COL > 100)	ks COLTR	1	370	0.592	6.884	-0.013
	MTB SO_4	2		0.924	1.156	0.715
	DOC	3		0.933	1.028	-0.088
all lakes	auto COLTR	1	175	0.665	6.972	-0.024
(excluding	MTB SO_4	2		0.705	5.341	0.233
Sudbury)	DOC	3		0.718	5.417	-0.106
stream sites	ks COLTR	1	394	0.722	6.397	-0.012
	MTB SO_4	2		0.932	2.154	0.651
	DOC	3		0.937	2.051	-0.089
stream sites (col < 30)	MTB SO_4	1	89	0.883	2.012	0.658
(col 30-100)	MTB SO_4	1	550	0.806	0.482	0.721
	ks COLTR	2		0.871	1.963	-0.029
	DOC	3		0.874	2.138	-0.135
(col > 100)	ks COLTR	1	361	0.598	6.935	-0.013
	MTB SO_4	2		0.930	1.096	0.723
	DOC	3		0.941	0.936	-0.135

do not dissolve in the solvent used in the extraction process, which resulted in higher recoveries of the chlorophyll pigments.

The Toronto lab conducted some preliminary comparison tests, and reported that recoveries were 50% and 35% higher for chlorophyll a and b, respectively. The tests showed a relative standard deviation of 5% at 205 μg/L. Based on these results, the LSB changed to the nylon filters for all analysis on June 13, 1985.

From June to August 1985, the DRC in association with the LSB, conducted a comparison study of the two filter types. The nylon filtered samples were also collected in duplicate to estimate analytical precision. The data included 32 samples from WRB-Phytoplankton Taxonomy and 209 samples from the DRC. Our results show a relative standard deviation of 184.6% and 100.0% for chlorophyll a and b, respectively. These results are significantly higher than precision on lab duplicates the LSB reported in June 1985. The linear regression results between the two filter types show very good correlation. The slope of the regression line however, indicates that the chlorophyll results using the nylon filters are 30-50% higher than the cellulose nitrate membrane filters, as found by the LSB's preliminary report. A summary of the regression analysis is shown in Table 2.6. The cellulose nitrate membrane filtered results were regressed as the dependent variable in all cases (to correspond to the regression analysis done by the LSB).

The results of the lineary regression done by both groups indicate that the 1985 to present chlorophyll data analysed with the nylon filters are not directly comparable to that collected over the previous 10 years. Analysis of the chlorophyll samples using nylon filters was suspended in September 1985. In June, 1986 the chlorophyll analysis was contracted to a private firm. The samples collected from September 1985 to June 1986 were analysed in late 1986. The method to correct the sartorius filtered chlorophyll data has not been derived. A complicating factor was the privatization of this analytical procedure. Questions concerning the compatibility of the process, the quality control process of the private lab and the merging of this data with the SIS data base were not addressed satisfactorily. The LSB resumed analysing the chlorophyll samples at the Rexdale lab in Toronto. All samples are filtered with nylon filters at the DRC field lab.

Table 2.6 Linear regression comparison of cellulose nitrate membrane filters and nylon filters used in the analysis of chlorophyll, (as reported by the DRC and the LSB).

testing agency	data section criteria	N	r	intercept	slope
DRC	all samples	240	0.963	0.613	0.262
	DOC 1-4 μg/L	29	0.932	0.694	0.078
	DOC 4-6 μg/L	19	0.892	0.622	0.266
LSB	Dorset samples	42	0.984	0.612	0.22
	WRB samples	109	0.907	0.778	0.10

2.2.2.3 Estimation of Colour

The analytical methodology for the estimation of colour was under review during the Fall of 1980. Before October 15, 1980, colour was estimated using the comparator disc procedure, and reported as "apparent" colour (COLAP). The range on an undiluted sample was 5-250 (Hazen Units) H.U., the detection limit was 5 H.U. and the precision was + or - 5 H.U. in the 5-20 H.U. range (OME 1975, OME 1981). On October 15, 1980 a colourimetric method using cobaltiplatinate standards was also used to estimate "true" colour. True colour (COLTR) only considers dissolved coloured substances and requires a correction for turbidity and particulates (Crowther 1977). The detection limit is 0 H.U. and the precision is + or - 0.1 H.U., with an unlimited range (OME 1981). The COLTR was calculated from a linear regression of colour absorbance versus a slope of COLTR measurements derived weekly from standards. Klett-Summerson (equipment manufacturer) suggested that the slope should be 1.35 however, field lab estimations showed that the value was 1.65. During October, 1980 these three methods were measured for all samples, (COLAP), COLTR (1.35), COLTR (1.65)). Table 2.7 summarizes the regression results between the different methods. The colour results reported in the DRC data base after October 15, 1980 are COLTR (1.65) reported now in true colour units, (TCU). Linear regression results indicated COLAP and COLTR (1.65) may vary by as much as 19 units.

Different selection criteria on the comparison data base yield regression coefficients with slopes and intercepts significantly different from 1.0 and 0.0, respectively. In order to compare the current colour data to data from other labs and historical COLAP data, correction factors must be applied. The different selection criteria summarized in Table 2.7 indicate that this process is not a simple one.

Problems relating to the analysis for colour have continued. The method change to "true" colour in October, 1980 resulted in more accurate data, but significant difficulties in analytical precision become apparent. During 1984 and 1985 a routine quality assurance replicate sampling programme monitored all sites. The data generated by this programme are discussed in Section 3 of this report. The results of these analyses indicate that the COLTR precision always exceeded the Water Quality published standard deviation limits (OME 1986). Table 2.7 summarizes the variation observed in the COLTR data during 1984, (QC data analysed for COLTR 1984-1987 are summarized in Table 3.1). This problem was discussed in an internal report to the LSB (Locke and Reid 1985). More stringent controls are now made in operator selection and for the auto-analysis standard settings.

The LSB also proposed the use of a full automated COLTR procedure (Cheung 1984). During the time period August to October 1985, the field lab

Table 2.7 Linear regression comparison of three colour estimation procedures (COLAP, COLTR (1.35) and COLTR (1.65), measured on water chemistry samples at the field lab in Dorset, October 1984.

regression variables independent	dependent	N	r	intercept	slope
COLTR (1.65)	COLAP	149	0.981	-12.631	0.807
COLTR (1.65)	COLTR (1.35)	132	0.999	0.073	0.805
COLAP	COLTR (1.35)	131	0.982	14.620	0.959
COLTR (1.65)	COLAP > 5 HU	91	0.981	-18.489	0.852
COLTR (1.65) < 70 HU	COLAP > 5 HU	32	0.713	- 2.551	0.523
COLTR (1.65) > 70 HU	COLAP > 5 HU	57	0.974	-19.203	0.859
COLTR (1.65)	DOC	86	0.979	1.901	0.081

tested both the Klett-Summerson (K-S) and an automated (auto) COLTR method on selected samples. These samples were chosen to cover the full analytical range of colour. Results show an extremely high correlation between the two results, but the slope and y intercept were significantly different from 1.0 and 0.0, respectively. The multiple linear regression equation for the auto COLTR, (the dependent variable) and the K-S COLTR was:

auto COLTR = 0.847 (K-S COLTR) - 2.512 r = 0.996

N = 587

The stepwise linear regression analysis for the auto COLTR, (the dependent variable) and the K-S COLTR and DOC was:

step 1: auto COLTR = 0.848 (K-S COLTR) - 2.524 r = 0.996

n = 578

step 2: auto COLTR = 0.673 (K-S COLTR) +

2.284 (DOC) - 6.117 r = 0.997

Although the correlation is very good, the slope of the regression (0.85) indicates that there is a large and systematic difference between the two measurements. Since we were already "correcting" the colour data to relate

the manual "true" colour to the "apparent" colour of pre-1980, an additional set of corrections seemed unwarranted.

2.2.2.4 Trace Metal Analytical Methodology

The analysis of trace metals such as aluminum, zinc, cadmium and lead have gone through considerable changes in the past 5 years. These parameters are usually in a 0-20 μg/L range, but analysis in the past has not been accurate at these levels of detection. Much of the reported data therefore, was below detection limits. Improved lab analytical techniques, (clean room) and the switch from the Inorganic Trace Contaminant (ITC) lab to the DRC has resulted in improved results.

In 1983, a comparison study between the ITC and DRC analyses of total zinc and aluminum showed poor correlation between the two labs' results, particularly for ZNUT. Table 2.8 summarizes the results of the regression analysis.

Evaluation of the ITC versus DRC analyses for trace metals continued in 1984. The Dorset lab analytical process underwent considerable change in November 1985. All precipitation and Sudbury lake samples were submitted in duplicate for zinc, lead and cadmium analysis. This study is ongoing as the Dorset lab continues to make improvements in analytical techniques. Table

2.9 summarizes the results of linear regression between the two lab's results. Many of the results reported by the ITC lab were below detection criteria, and were not included in the regression analysis. The comparison for each of the three metals shows that the Dorset analytical procedure consistently reports lower values than the Toronto lab. Because the detection limits in the Toronto lab are higher, the Toronto lab reports many more values below detection limits, (summarized in Table 2.9).

2.2.3 Collection Methods

The types of collection methods used by the Limnology Unit of the DRC are continually monitored. When the sampling methods changed, or when different organizations supported the collection of the same data, the sample collection methods were compared. This section presents the results of some comparisions for precipitation, lake and stream sample collection.

2.2.3.1 Precipitation Sample Collection (DRC)

Two bulk precipitation collectors were monitored at the Paint Lake study site from May 1979 to May 1984 to estimate collector precision. Table 2.10 summarizes linear regression analysis results between the parameters measured at both sites. Correlation between the two collectors was good for

Table 2.8 Linear regression comparison of the Dorset lab and the Inorganic Trace Contaminent lab (ITC) analysis of total zinc (ZNUT) and aluminum (ALUT), 1983 data. The Dorset data was the dependent variable in the regression analysis in all comparisons.

data selection criteria	N	r	intercept	slope	95% CI about the slope	
Zinc						
all samples	209	0.002	5.606	0.001	-0.038	0.039
COLTR < 70	106	0.057	5.139	0.033	-0.078	0.143
COLTR > 70	110	0.271	4.097	0.179	0.058	0.301
Aluminum						
all samples	277	0.839	12.743	0.942	0.870	1.015
COLTR < 70	138	0.823	15.449	0.827	0.731	0.923
COLTR > 70	139	0.835	16.057	0.970	0.863	1.078

Table 2.9 Linear regression comparison of the Dorset lab and the Inorganic Trace Contaminant lab (ITC) for ZNUT, PBUT and CDUT (AAS and ASV), 1985-1987 data. The Dorset lab data is the dependent variable in all comparisons.

parameter	N	r	intercept	slope	95% CI slope		detection limits Dorset (μg/L)	detection limits ITC (μg/L)
ZNUT	105	0.706	5.503	0.209	0.168	0.250	0.50*	1
PBUT	44	0.447	2.007	0.167	0.063	0.271	0.05*	3
CCUT	27	0.981	0.504	0.597	0.549	0.646	0.50	1
CDUT								
AAS	8	0.614	0.366	1.060	-0.301	2.421	0.001*	0.3
ASV	19	0.761	-0.099	0.661	0.373	0.949	0.01	0.3
Dorset (AAS vs ASV) ** CDUT	78	0.780	0.257	1.723	1.407	2.40	as above	

* These detection limits changed for the Dorset lab in November 1986 from 0.5 to 0.2 for ZNUT and from 0.05 to 0.1 for PBUT, and from 0.001 to 0.01 for CDUT (AAS) January 1, 1987.

** CDUT analysed by AAS at Dorset is the dependent variable in this regression. Both AAS and ASV are analytical methods used to detect CDUT by the Dorset lab.

most parameters. High ALUT, ZNUTand NNTKUR are typical contaminants to precipitation samples. The first group of parameters was edited for obvious sample contamination bias prior to regression comparison. Samples for each of the two sites were not collected in duplicate. It remains unclear whether the extreme variability at the higher range of values is due to sample contamination or analytical variability. Analytical variation is often higher at values closer to detection limits. In May 1984 one of the duplicate collection samplers was discontinued.

2.2.3.2 **Precipitation Sample Comparison Between DRC and ARB**

Both the Dorset Research Centre (DRC) and Air Resources Branch (ARB) collect precipitation samples at the Paint Lake site at the DRC. The DRC collects bulk precipitation, monitored on an approximate weekly basis (Locke and Scott, 1986). The ARB collects event precipitation, monitored on a daily basis (OME, 1984). There are several other organizations collecting meteorological data at this site, including precipitation chemistry.

A comparison of precipitation chemistry between the DRC and the ARB was made during the time period November 23, 1982 to December 13, 1984. The ARB data was also compared to the WRB Phytotoxicology samples collected at this site during the same time period.

Table 2.10 Linear regression comparison of two bulk precipitation collectors at the Paint Lake site.

parameter	N	r	intercept	slope	95% CI about the slope	
Note: This parameter group was edited for obvious sample contamination and not presumed analytical error prior to linear regression analysis. ZNUT shows significant correlation problems between the two collectors especially in the > 20 μg/L analytical range. The variation is uniformly scattered between the two collectors.						
ALUT	152	0.838	6.032	0.827	0.740	0.914
CAUR	152	0.986	0.030	0.978	0.951	1.005
CLIDUR	153	0.908	0.015	0.891	0.825	0.957
NNHTFR	153	0.945	19.595	0.940	0.886	0.992
NNOTFR	153	0.994	0.949	1.004	0.986	1.022
NNTKUR	145	0.932	45.484	0.887	0.830	0.944
PPUT	142	0.952	1.990	0.884	0.836	0.931
SI03UR	155	0.979	-0.003	0.999	0.966	1.003
ZNUT (all data)	129	0.465	12.925	0.409	0.273	0.546
ZNUT (<20 μg/L)	74	0.829	0.794	0.897	0.755	1.040
Note: This parameter group was not edited prior to linear regression analysis.						
MGUR	157	0.989	-0.0001	0.991	0.967	1.014
H^+	16	0.982	2.492	0.971	0.942	1.001
ACDT	66	0.972	0.243	0.929	0.873	0.986
ALKT	10	0.937	-0.314	1.479	1.029	1.928
ALKTI	78	0.974	0.048	1.015	0.961	1.069
COND	160	0.989	1.389	0.995	0.972	1.018
DOC	158	0.912	-0.097	1.247	1.158	1.336
FEUT	158	0.878	5.821	0.996	0.910	1.082
FFIDUR	42	0.990	-0.031	0.972	0.928	1.016
KKUR	157	0.851	0.017	0.805	0.726	0.884
MNUT	158	0.976	0.097	1.039	1.003	1.076
NAUR	157	0.823	0.007	0.988	0.879	1.096
SS04UR	157	0.991	0.053	0.978	0.958	0.999

The results of this comparison study were analysed by both the DRC and ARB in September 1986. The sample depths compared very well (slope of regression line 1.01 and r = 0.989) after 2 flyers were removed from each data set. The comparison of SO_4 data shows a slope of the regression line of 1.17 (significantly > 1) and in 80 of 81 data pairs the DRC figure is higher. Rather than concluding that the DRC bulk collectors are overestimating the deposition or concentration of SO_4, these higher values indicate a very realistic estimate of the deposition of wet SO_4 plus dry (particulate SO_4). There were serious analytical problems with the ARB pH measurements made at Dorset using the Ingold electrode system. The LSB at Dorset made thorough comparisons between 5 separate pH meters and probes. The problems with non-standard pH analytical methods were resolved. The comparative analysis for the NO_3 and NH_4 data was not so conclusive. Both event (ARB) and bulk (DRC) collectors appear to have several outliers in their data sets, neither one of which may be sampling reliable measurements.

The comparison data set indicates the DRC gauge depths and sample depths by volume were almost identical (see discussion in Section 2.2.3.3 on the comparison of nipher depths versus sample volume). The DRC and ARB gauge depths also compared well, especially after 4 points were removed from the regression (2 for each group). The slope of the regression line was 1.01 and the correlation excellent (r = 0.989).

2.2.3.3 Precipitation Depth Estimates

Two estimates of the depth of precipitation are routinely measured. The volume of precipitation is recorded for every sample collected and is entered to the data base with the sample chemistry data. The depth of precipitation is also measured for every bulk event, and it is this depth that is primarily used for deposition calculations. The volume data, coupled with the area of the collector is used for cross-checking and also as a back-up in the event that the gauge depth value is missing.

A standard rain gauge was used to record precipitation depth from May to November from 1976 to May 1984. Snow depths used in deposition calculations were measured from 1976 to 1978 with a snow board and ruler. From 1978 to 1984, snow samples were melted and volumes measured to obtain water equivalent depth, using either Nipher gauges. Currently Belfort gauges are used to record both hourly and daily total precipitation depth. Comparisons between the gauge depth and the sample volume show the confidence placed on the gauge depth used to estimate the precipitation loading. Table 2.11 summarizes the linear regressions run on these two estimates. Various subsets of the data were evaluated separately to isolate any gauge type effect. A regression was also done on the complete data set (1977 to 1985) to compare the gauge depth as a measurement type compared

to the sample volume. The sample volume was regressed as the dependent variable in all regressions.

The slopes of all the regression lines are less than 1.0, indicating that the volume always underestimates the depth. Two of the stations (HPP2 and HYP2) have slopes that are significantly less than 1.0 and the intercepts are both highly positive.

Some estimation of collector efficiency can be seen by the comparisons between different precipitation types. The slopes are all much less than 1.0 but the intercepts are generally close to zero with correlation coefficients of greater than 0.9. Currently Belfort gauges record the depth used in loading calculations and the volume of sample collected is used only as a backup and for comparative evaluation in data edit procedures.

Table 2.11 Linear regressions comparison of the precipitation sample volume (dependent variable) versus the precipitation gauge depth as an estimate of precipitation amount.

data selection criteria	N	r	intercept	slope	95% CI about the slope	
All sites, all years	1141	0.956	0.524	0.616	0.899	0.932
HPP	223	0.925	-0.411	0.906	-	-
HPP2	95	0.975	2.635	0.865	-	-
HYP	75	0.974	-0.62	0.938	-	-
HYP2	89	0.963	1.435	0.893	-	-
PCP	132	0.972	0.516	0.937	-	-
PCP2	89	0.976	1.260	0.906	-	-
PT1P	274	0.960	0.535	0.917	-	-
PT2	164	0.977	-0.108	0.947	-	-
Gauge Type Effects:						
Rain Collection 1976-1086	663	0.953	0.088	0.240	0.233	0.245
SRG gauge (rain) May-Oct 76-84	557	0.950	0.010	0.241	0.234	0.247
Winter snow collection	488	0.981	-0.081	0.228	0.220	0.232
Nipher gauge (snow) Nov-Apr 78-84	298	0.961	-0.158	0.229	0.222	0.237
Snow ruler Winter 76-78	38	0.907	-0.309	0.177	0.150	0.205
Belfort gauge 84-Present	221	0.967	0.314	0.215	0.207	0.222

2.2.3.4 Streams Dissolved Oxygen Sample Collection

The collection of a water sample for oxygen analysis must be done without aerating the sample. All routine stream chemistry samples are taken at the notch of the control structure. There is a continuous flow of water at the notch and the sample container may be filled without disturbing the stream bed. This sampling method is inappropriate for an oxygen sample however, as the water is usually aerated as the flow cascades over the control notch. A sampling comparison study was made in March of 1982 between oxygen samples taken at the notch (independent variable) and samples taken in the pool behind the control. Samples taken here were submerged in the pool, and the water allowed to seep into the container with no aeration. The linear regression equation calculated from 50 data pairs was:

pool = notch (0.9774) + 0.1482 r = 0.990

N = 50

The regressions were also run separately on the two different kinds of control structures, weirs and flumes. These structures are described in Locke and Scott (1986). Those equations calculated were:

Weirs: pool = notch (0.994) - 0.003 r = 0.998

N = 29

Flume: pool = notch (0.925) + 0.658 r = 0.965

N = 21

These results indicate that samples taken at the pool have slightly lower oxygen values than those taken at the notch. The flume is also shown to aerate the samples more than the weir. These results are consistent with the configuration of the sampling locations. The sampling of oxygen is done routinely from the pool of all stream controls.

2.2.3.5 **Hydrology - Measurement of Stream Flow**

Discharge measurements from streams are taken by one of two methods, depending on flow. At flows less than 8 L/sec, the entire volume of the stream is caught in a container for a measured period of time and discharge calculated. Flows of more than 8 L/sec are calculated by combining the measured velocity of the water with the cross-sectional area of the stream (Locke and Scott, 1986). The velocity is measured using either a Teledyne Gurley Pygmy Model 625, an Ott C32 or an Ott 31 current meter. Replicate measurements of flow measured by the three current meters were collected in October 1980. The results showed the Ott 31 to be less accurate in the lower flows found in small head water streams (standard deviation > 5 L/sec and mean significantly different at 1 and 5% levels).

Electronic gauging equipment was tested by the DRC in the fall of 1982. A Marsh-McBirney 201M and Montedoro-Whitney PVM-2 were used to measure flows using both AC and DC power sources. Teledyne-Gurley (Pygmy), Ott (C32) and bucket were also used to compare standard gauging equipment. A variety of flow conditions for 13 different sites over 24 sampling comparisons were compared in this study. Six replicates were taken for each gauging instrument.

A bucket may be used to measure flows less than 20 L/sec. This method is considered the most accurate. The flows measured by bucket were significantly higher than all other gauging methods. The Pygmy current meter is not accurate at flows greater than 30 L/sec while the Ott current meter is not accurate at flows < 10 L/sec. The Ott meter values were always significantly higher than the Pygmy values and both electronic meters recorded lower flows than the Ott and Pygmy. The two electronic meters were compared for both DC and AC power sources. The AC current supply values showed high standard deviations and seem to have been affected by metal in the structure. The results of these comparisons clearly shows the importance of selecting the appropriate gauge type for flow conditions. The electronic gauging equipment was not sensitive enough to low flows. The interference with metal in the structure could not be isolated and all data values were suspect. Currently Pygmy meters are used for low flows and Ott 31 current meters for high flows.

2.2.3.6 Lakes - Estimation of the Euphotic Zone

The euphotic zone of lakes is estimated by a Secchi disc (Locke and Scott, 1986). The conventional use of this instrument provides an estimate of roughly half of the euphotic zone, or zone of maximum light penetration. These measurements can be affected by weather variations, surface water conditions, water colour and turbidity and sampler variation. During the ice-free season of 1982 and 1983, a light profile was recorded on selected lakes using a Li-192 cosine-corrected quantum sensor. The lower limit of the euphotic zone was the depth where light was 1% of the readings taken just below the surface. A comparison was made between the depths estimated by the Secchi disc and the light meter. Table 2.13 shows the results of linear regression analysis between the two methods. The Secchi disc depth was regressed as the independent variable in all cases. The depth of the euphotic zone estimated by the Secchi disc was also calculated at 2.5 times, and included in the regressions. The depth of the bottom of euphotic zone can also be expressed as a strata 'range' to the nearest even metre interval. This interval division is used by field crews, when volume weighting lake strata from morphometric information for sampling strategies.

The relationship between the 1% of surface light level by extinction and factoring the Secchi disc depth is not a close one, and is dramatically affected by the light attenuation characteristics of each lake. Given this fact and the

inherent variation of Secchi disc observation, estimation of the euphotic zone by light meter measurement appears to be more accurate. The slopes of all the regression equations all show that the 1% light depth as recorded by the light meter estimates a shallower euphotic zone, presumably caused by 'doubling' error in Secchi disc multiplication. Linear regressions were done on each of the study lakes, but only Chub Lake showed a significant correlation. The other lakes exhibit poor correlation primarily due to low variation in the data. The best correlation occurs when comparing the 1% light depth and 2X Secchi depth 'ranges'. This is due to the rounding up of all depths to the nearest even metre, causing a smoothing to the data variation. This closely approximates the sample collection procedure (Locke and Scott, 1986). The Secchi disc data in the comparison also showed approximately twice the standard deviation to the 1% depth data. Any errors in measuring depths with the Secchi disc are compounded by the 2X factoring process. Light meter profiles are not possible for aircraft sampling due to aircraft interference. The inconclusive comparison results, and limnological convention make the Secchi disc the preferred sampling methods.

Table 2.12 Linear regression comparison of the estimation of the euphotic zone by the Secchi disc (independent) and a light profile using a Li-192 cosine-corrected quantum sensor (dependent).

data selection criteria	N	r	intercept	slope	95% CI about the slope	
strata 'range' by 2X Secchi:						
all lakes	184	0.840	0.076	0.909	0.824	0.994
Chub Lake	31	0.670	1.801	0.539	0.312	0.766
meter depth by 2X Secchi:						
all lakes	184	0.830	-0.047	0.895	0.807	0.983
Chub Lake	31	0.711	1.937	0.433	0.270	0.595
1% depth by 2.5X Secchi:						
all lakes	184	0.830	-0.047	0.716	0.646	0.787
high colour lakes*	99	0.678	2.319	0.530	0.404	0.656
low colour lakes	85	0.408	7.190	0.510	0.280	0.741

* The colour differentiation was made on the basis of annual averages. High colour lakes included Crosson, Chub and Dickie and the low colour lakes included Blue Chalk, Red Chalk Main and East basins and Plastic.

2.2.3.7 Phytoplankton Collection Methods

The Secchi disc estimation of the euphotic zone is used on all study lakes as a matter of convention. A special study was initiated on Chub, Plastic and Red Chalk Main Lake during the ice-free seasons from 1983 to 1985. When the euphotic zone depth derived from the calculation of twice the Secchi disc differed from the 1% light depth, separate phytoplankton collections were made from the two zones. The results of this comparison have been analyzed for a separate report by Norm Yan (1986).

2.2.3.8 Lake Water Sample Collection Methods

Samples for chemical analysis are taken with a peristaltic pump and 1 mm id tygon tubing. The tubing is lowered to intervals from the top to the bottom, at the deepest spot in the lake. Aliquots of water proportional to the volume of stratum represented are removed from each depth and added to a carboy to obtain a volume-weighted, composite sample (Locke and Scott, 1986). Some lakes are not sampled on a routine basis, or may only be sampled once. These lakes are often sampled using a 6 metre 1 inch tube. This tube is lowered vertically through the first 6 metres of the lake and pinched off at the top. The lower end is then brought to the surface and the contents of the tube poured into a carboy. This method provides for a 0-6 metre tube

composite sample. A comparison was made on 12 lakes in August, 1984 of samples taken with a tube composite and a volume-weighted epilimnion sample, (not necessarily to the same depth). The depth of the epilimnion is estimated by a temperature profile. Table 2.14 shows the results of this comparison. Since both the methods are routinely used to 'estimate' a measure of chemical concentration, the different depths of samples are ignored in this comparison.

Most of the chemical parameters sampled compared well between the two sampling methods. COLTR and ALUT however show poor correlation and significant slopes and intercepts. This may be due to the poor replicate capability of the analytical procedure at these levels and for these types of samples rather than any bias between the two methods (see Section 3 for precision data for these parameters). The composite samples are used for lake survey studies involving large numbers of lakes, and for sampling shallow littoral zones for which no volumetric data is available.

2.2.3.9 **Lake Temperature Profile Measurements**

Temperature profiles are recorded on study lakes using submersible temperature probes electronically connected to a meter readout unit, with a

Table 2.13 Linear regression comparison of tube composite water samples (dependent) and epilimnion volume-weighted water samples.

parameter	N	r	intercept	slope	95% CI about the slope	
pH	12	0.977	-0.027	1.011	0.857	1.164
ALKTI	12	0.997	0.022	0.993	0.934	1.051
ALKT	12	0.988	0.111	0.969	0.830	1.077
COLTR	12	0.817	1.795	1.385	0.696	2.073
COND	12	0.811	1.690	0.948	0.466	1.429
CAUR	12	0.957	0.160	0.924	0.727	1.123
MGUR	12	0.965	0.028	0.949	0.766	1.131
NAUR	12	0.986	0.037	0.975	0.858	1.092
KKUR	12	0.993	0.027	0.972	0.892	1.051
CLIDUR	12	0.978	0.077	0.840	0.713	0.967
SS04UR	12	0.860	0.190	1.011	0.589	1.432
DOC	12	0.956	0.433	0.871	0.683	1.060
ALUT	12	0.632	6.745	0.381	0.051	0.711

cable length of approximately 50 m. From 1976 to 1982 Montedoro-Whitney thermistors were used to record temperature profiles in the study lakes. In 1982 a new Flett thermistor replaced the previously used instrument. The Montedoro-Whitney unit was housed in a large metal drum which revolved as the cable was raised or lowered. Rechargeable nickel cadmium batteries were used. The Flett thermistor is compact and light-weight with a LED readout and a 9-volt transistor battery. A comparison was made between two Flett thermistors and the Montedoro-Whitney. Linear regression results indicate that there is high correlation between the two methods (0.990 and 0.973) within the 0-5°C range (comparison was done February, 1983). The slopes were 0.998 and 1.019 with intercepts of -0.010 and -0.189, respectively. The sample sizes for each of the two comparisons were 64 and 194. Based on these tests results and subsequent excellent calibrations of the Flett thermistors in the 0-25°C range, the use of Montedoro-Whitney thermistors was discontinued.

2.2.3.10 **Zooplankton Collection Methodology**

The lake sampling station location for zooplankton was evaluated in 1982. Zooplankton patchiness experiments were conducted in Red Chalk Lake during the ice-free sampling season in 1982. Five additional sampling stations were sampled with a flowmeter tow-net system (described in Locke and Scott, 1986). The analysis of these data is presented in Yan (1986).

Volume weighted versus non-weighted sampling techniques for zooplankton have also been evaluated. Both types of sampling were done on Red Chalk, Chub and Plastic Lakes from 1982 to 1984. These data are also presented in Yan (1986).

2.2.3.11 Sample Container Evaluations

The sample container types and the cleanliness of these containers are under continual revision. One of the most notable changes has been the shift away from field laboratory prewashing of reusable sample containers to single-use recyclable or throw-away containers. The latter were routinely in use for the majority of parameters after June 1, 1982. The quality of these containers has been evaluated by submitting distilled water blanks to the lab for analysis and by comparing two or more containers with the same water sample. Precipitation sample containers, because of a very dilute water chemistry, are especially scrutinized on a routine basis.

3. QUALITY CONTROL REPLICATE PROGRAMME 1983-1987

3.1 Experimental Procedures

A comprehensive programme began in 1983 to evaluate the contribution of the collection and analytical sources of variation inherent in our data. All chemical parameters and field techniques used at that time were 'replicate' sampled at all routinely monitored sites on a rotational basis. The 'replicate' process entailed the separate collection of 3-10 samples additional to the regular sample.

The range of the quality control data replicates for each of the lake, stream and precipitation and lake profile sites are summarized in tables in Appendixes 8.2, 8.3, 8.4 and 8.5. The mean, standard deviation, coefficient of variation and number of samples per replicate data are not published in this report. The data is available for reference at the Dorset Research Centre. Table 3.1 contains mean sample type and average DRC precision statistic for each parameter. The sampling procedures used in this replicate study are identical to those used in the routine monitoring programme described in Locke and Scott, 1986. These precision figures can therefore be applied to the data base collected as part of the Limnology Unit's studies in Muskoka/Haliburton.

This replicate sampling programme that began in 1983 is still in operation at the present date. All major study lakes were replicated starting in June, 1983 on a

rotating basis. In 1984 all streams and precipitation sites were replicate sampled as well on a rotating schedule basis. In June, 1986, after preliminary analysis of the data, three sites were selected to continue the replicate sampling. The three sites are Clearwater Lake in Sudbury and Dickie Inflow #6 and Harp Outflow and cover the widest analytical range for most of the parameters sampled. These sites will continue to be tested for sampling and analytical precision as part of the DRC quality assurance programme.

The replication of routine sampling procedures varied a little for each of the three sample types. The samples for each of the replicated streams were collected sequentially from the designated sampling site in addition to the regular sample. The precipitation samples were aliquoted in replicate from a single bulk sample. The lake chemistry replicates were collected by repeating the entire sampling procedure 5 times in addition to the regular sample. The lake profile samples for DIC, oxygen and pH were also collected by repeating the entire sampling procedure in addition to the regular profile samples. The profile data have been statistically evaluated for each depth replicated, in the same manner as the chemistry samples.

3.2 Statistical Results and Evaluation

Table 3.1 summarizes the individual sample type means as well as an all sample average mean. These precision figures can be compared to the performance report produced by the Water Quality Section, LSB, (1984, 1985, 1986). Certain parameters

exceed the analytical precision reported by the LSB. For some Toronto parameters LSB reports precision data for all samples coming to their lab, not just from Dorset. This may be important if Dorset samples are in a lower (0-20%) of analytical range. Error may also be introduced during the sampling procedure. This may be especially true in replicating lake profile and strata samples repetitively at the same spot in the lake, due to top to bottom mixing inadvertently introduced by the replicate sampling procedure. Table 3.2 lists the parameters that deviate from the reported LSB precision criteria.

Appendix 8.1 lists standard parameter abbreviations used in this document. Site abbreviations are listed at the beginning of Appendices 8.2 through 8.4. Appendix 8.2, 8.3 and 8.4 summarize the range of quality control replicate data by parameter.

Table 3.1 Quality control replicate statistics of water chemistry samples for study lakes, streams and precipitation sampling sites at the Dorset Research Centre, 1983-1987.

* sample type	parameter	** number of sites	*** mean	mean standard deviation	mean coef of var (%)
1	ALEXCV	1	3.171	1.196	18.205
2		2	65.708	2.353	8.962
3		0			
ALL		2	34.440	1.775	13.584
1	ALKT3	1	7.927	0.156	2.016
2		3	10.133	0.197	2.055
3		0			
ALL		2	9.030	0.176	2.036
1	ALNDCV	1	137.700	2.030	1.495
2		2	71.896	2.325	7.930
3		0			
ALL		2	104.798	2.176	4.713
1	COND25	16	31.117	0.226	0.685
2		30	40.634	0.445	0.853
3		5	44.167	0.656	1.526
ALL		4	38.639	0.442	1.021
1	ALKT	16	3.438	0.091	3.505
2		29	9.886	0.297	3.466
3		6	0.033	0.011	14.307
ALL		3	4.452	0.133	7.093
1	ALKTI	16	1.658	0.114	14.911
2		30	7.433	0.125	13.504
3		6	-4.497	0.091	2.665
ALL		3	1.531	0.110	10.360

Table 3.1 (cont'd)

* sample type	parameter	** number of sites	*** mean	mean standard deviation	mean coef of var (%)
1	ACDT	0			
2		0			
3		4	4.658	0.217	5.133
ALL		1	4.658	0.217	5.133
1	pH	16	5.729	0.039	0.681
2		30	5.668	0.022	0.402
3		6	4.120	0.016	0.376
4		8	5.817	0.084	1.417
ALL		4	5.334	0.040	0.719
1	FFIDUR	21	42.332	1.138	3.032
2		28	47.931	0.612	1.277
3		6	4.794	0.989	18.886
ALL		3	31.686	0.913	7.732
1	COLTR	20	20.953	2.393	18.388
2		30	123.232	3.837	7.018
3		0			
ALL		2	72.093	3.115	12.703
1	NNHTFR	18	23.859	2.725	26.605
2		26	34.204	3.212	17.822
3		5	305.090	4.666	1.758
ALL		3	136.051	3.534	15.395
1	NNOTFR	16	58.982	2.490	7.586
2		30	64.177	2.612	9.004
3		6	449.808	7.984	1.464
ALL		3	190.989	4.362	6.018

Table 3.1 (cont'd)

* sample type	parameter	** number of sites	*** mean	mean standard deviation	mean coef of var (%)
1	NNTKUR	20	247.070	15.674	7.016
2		13	318.881	11.456	3.426
3		2	240.125	8.191	4.358
ALL		3	268.692	12.016	4.933
1	DIC	4	1.613	0.077	5.721
2		2	2.091	0.063	4.429
3		0			
4		5	1.999	0.082	4.766
ALL		3	1.901	0.074	4.972
1	ALUT	12	63.747	3.294	7.557
2		12	96.481	6.161	13.204
3		6	15.752	6.214	30.285
ALL		3	58.660	5.223	17.015
1	PPUT	10	8.257	0.609	8.692
2		2	38.069	1.218	8.136
3		0			
ALL		2	22.163	0.914	8.414
1	DO	0			
2		21	8.679	0.266	4.330
3		0			
4		11	5.915	0.422	19.850
ALL		2	7.297	0.344	12.090
1	CUUT	1	0.043	0.002	4.412
2		2	0.002	0.000	0.000
3		0			
ALL		2	0.023	0.001	2.206

Table 3.1 (cont'd)

* sample type	parameter	** number of sites	*** mean	mean standard deviation	mean coef of var (%)
1	NIUT	1	0.187	0.006	2.995
2		0			
3		0			
ALL		1	0.187	0.006	2.995
1	ZNUT	12	5.322	1.716	30.787
2		10	8.087	1.453	11.308
3		6	11.153	1.348	27.107
ALL		3	8.187	1.506	23.067
1	CDUT	1	0.227	0.052	17.555
2		2	0.044	0.053	90.292
3		0			
ALL		2	0.135	0.053	53.924
1	PBUT	1	0.003	detection limits	
2		2	0.510	0.080	26.717
3		0			
ALL		2	0.256	0.080	26.717
1	CAUR	24	2.600	0.076	2.700
2		28	4.030	0.297	6.989
3		6	0.251	0.007	15.848
ALL		3	2.294	0.127	7.579
1	MGUR	24	0.704	0.018	2.461
2		16	0.968	0.025	3.842
3		6	0.053	0.002	0.392
ALL		3	0.575	0.015	2.232

Table 3.1 (cont'd)

* sample type	parameter	** number of sites	*** mean	mean standard deviation	mean coef of var (%)
1	NAUR	24	0.763	0.026	3.377
2		16	0.892	0.016	3.349
3		5	0.050	0.005	13.606
ALL		3	0.568	0.568	6.777
1	KKUR	24	0.410	0.010	2.431
2		16	0.426	0.012	4.719
3		6	0.047	0.009	34.098
ALL		3	0.295	0.010	13.749
1	CLIDUR	24	0.752	0.045	10.908
2		17	0.810	0.038	8.120
3		6	0.113	0.010	14.289
ALL		3	0.558	0.031	11.106
1	SS04UR	24	7.062	0.141	2.069
2		16	7.183	0.181	3.158
3		6	2.713	0.015	0.534
ALL		3	5.653	0.112	1.920
1	SIO3UR	23	1.086	0.030	2.606
2		16	2.258	0.046	2.136
3		2	0.015	0.000	0.000
ALL		3	1.120	0.025	1.581
1	DOC	24	3.415	0.115	3.983
2		16	12.141	0.261	2.377
3		6	0.803	0.030	4.462
ALL		3	5.453	0.135	3.607

Table 3.1 (cont'd)

* sample type	parameter	** number of sites	*** mean	mean standard deviation	mean coef of var (%)
1	FEUT	23	0.502	0.032	12.452
2		28	0.663	0.042	9.417
3		2	0.019	0.003	19.712
ALL		3	0.395	0.026	13.860
1	MNUT	24	0.072	0.002	4.409
2		16	0.068	0.007	5.703
3		0			
ALL		2	0.070	0.005	5.056
1	ALDSE	0			
2		8	8.125	1.818	26.665
3		0			
ALL		2	8.125	1.818	26.665
1	ALNDSE	0			
2		8	63.200	7.115	14.289
3		0			
ALL		2	63.200	7.115	14.289
1	pF	0			
2		8	5.279	0.029	0.547
3		0			
ALL		2	5.279	0.029	0.547

* 1 = Lakes, 2 = Streams, 3 = Precipitation Sampling Stations, 4 = Lake Profile Samples

** Each site will represent 3-10 replicates, so that the sample size is a reference to the number of sample sites not samples taken.

*** This value is a mean of the mean of the replicates and is shown here to indicate the general analytical range of the samples. The actual data is available from the DRC.

Table 3.2 Chemical parameters replicated in the Quality Control Replicate program at Dorset that exceed Lab Services Branch (LSB) reported precision criteria.

parameter	analytical range (units)	sample type	mean standard deviation (DRC)	mean standard deviation (LSB)
COND25	20-50 µmhos/cm	PRECIP	0.656	0.47
FFIDUR	30-50 µg/L	LAKES	1.138	0.87
	0-10	PRECIP	0.989	0.48
COLTR	10-25 TCU	LAKES	2.393	0.40
	50-100	STREAMS	3.837	2.00
NNHTFR	0-25 µg/L	LAKES	2.725	1.17
	25-50	STREAMS	3.212	0.89
NNOTFR	250-500 µg/L	PRECIP	7.984	4.20
DIC	1-2 mg/L	LAKES	0.077	0.033
		PROFILES	0.082	0.033
FEUT	0.5-1.0 µg/L	LAKES	0.032	0.016
	0.5-1.0	STREAMS	0.042	0.016
PPUT	20-100 mg/L	STREAMS	1.401	0.7
ALUT	25-100 µg/L	STREAMS	6.161	4.3
	10-25	PRECIP	6.214	2.6

3.3 Long-term Trend Evaluation

A study began in June, 1986 to evaluate analytical error 'between runs', for different lab calibrations. Large sample volumes were obtained from three of our study sites and placed in the refrigerator. Samples were submitted in duplicate every two weeks for a selection of parameters, some of which were known to be perishable.

The original collection volume was sufficient to run the experiment for a six-month time period. This study was repeated for a second six-month time block. Results from this study indicate that for some parameters there is significant variation between the duplicates as well as between the analytical 'runs'. Variation due to perishability can be determined by plotting data over time. For the second time run, many of the highly perishable parameters were not submitted (DIC, NNOTFR, NNHTFR, NNTKUR, COLTR and DO). Many of the parameters that showed significant variation in the first round were sampled with more stringent controls. ALUT, ALEXCV, ALNDCV, FEUT and MNUT were kept in a special acid-washed container. ALKT3, ALKT, ALKTI and PPUT all showed significant variation and were monitored in the second study. The final results from both of the time-runs will be published in a separate QC data report.

3.4 Recommendations/Future Plans

The chemical parameters identified in Table 3.2 are outside the acceptable precision criteria. These parameters will continue to be monitored under the present analytical procedure. Every effort will be made to isolate the source of error and to adjust the sampling or analytical methodology accordingly.

Several of the analytical methodology studies summarized in this report have resulted in new and better technology development. The sulphate, colour and trace metal analysis are examples of parameters where analytical methodologies did not meet acceptable precision criteria, and changes were made to improve the reported data.

4. DATA MANAGEMENT

4.1 Scope

The responsibility of data management for the DRC rests first with the data manager and the computer support group and secondly with individual users. A data management working group continually reviews the scope and organization of the access and retrieval with the data bases now established on both the mini and micro computers for the site. The involvement of the Quality Assurance Management Programme is an integral part of this working group.

4.2 Data Base Storage

All of the chemical data that are collected as part of the Limnology Section's programmes are processed using the Sample Information System (SIS). The SIS is a general system designed to fulfil the data storage and retrieval needs for the Ministry of the Environment as a whole. Periodic transfer of sample submission information and chemistry results are made from the LSB to the SIS. In this way the SIS is updated and final reports and data files can be generated on a routine basis.

From 1976 to 1982, data was entered to the SIS via keypunched cards by the Systems Operation Section of the Financial and Administrative Services Branch. In 1982 the Laboratory Information System (LIS) was developed to provide data management

and improved sample submission procedures. This system receives submission information and routes samples to appropriate laboratory workstations. The LIS also inputs and stores the subsequent chemical analysis with the appropriate submission data. This information is input to the SIS at regular intervals to maintain and update the water chemistry data base.

The computer facilities at the DRC have undergone considerable upgrading since the beginning of the study. The procedures for sample submission and data entry have also changed markedly. The sample submission procedures are documented in OME (1976), OME (1982), OME (1984), OME (1985), Nicolls et al. (1986) and McCormick (1988). From 1976 to 1982, three desk-top Hewlett-Packard (HP) 9845 terminals were used to enter and verify the chemical data. The data were reported on field sheets by the LSB. The data files were stored on floppy discs and were periodically (monthly), transferred to the SIS via nine-track tapes. From 1982 to 1985 sample submissions were sent to the LSB in Rexdale weekly for entry to the LIS. The Limnology Unit at the DRC acquired a HP-1000 mini computer in 1982. Additionally the DRC has a number of personal computers that can either 'stand alone' or function as HP-1000 terminals. In 1985 the LSB acquired a HP-3000 computer system for use at the DRC in sample submission and chemical analysis input to the LSB. Weekly data transfer of approved sample submission sets is made through LIS to the SIS Downsview computer system.

From 1976 to 1988 data were retrieved from the SIS on nine-track tapes as required. The site data base was then stored on these nine-track tapes accessed by site developed software. Currently the data are retrieved weekly from the SIS on nine-track tapes and appended to the site data base stored on a dedicated 80386 micro computer. The data store incorporates an ORACLE relational data base management system and was operational in 1988. Only authorized individuals can make changes to the data base. Access to the data is also restricted to selected individuals. Data can be transferred from ORACLE to the HP-1000 or personal computers for statistical and graphical analysis. Data edit procedures are run on all data before it is released for any data requests (Locke, 1990). There are several statistical and graphical software packages available on-site. Much of the advanced data manipulation is enhanced by the development of software applications by DRC computer staff. Upgrading feasibility studies are continually under review as new technology becomes available. A major criteria in any upgrade is to ensure that the integrity of the data base is provided for. Access to this shared resource must be handled in an efficient and accurate manner. The site meteorological, hydrological and biological data bases will also be transferred to ORACLE data base systems by 1990. Procedures to update, edit and utilize all DRC data bases are standardized and well documented (LaZerte, 1989).

4.3 Data Evaluation

Data collected as part of the Limnology Section's programmes are subject to rigorous quality control/quality assurance procedures. It is the responsibility of the project leader of each of the section's projects to ensure that the data collected as part of that project are edited properly. Many techniques are used to assure the quality of the reported data. The calculation of charge balances, ionic strengths and theoretical estimates of measured parameters are all important ways to identify inconsistencies in the data. Graphical display, regression of theoretical versus measured and data printouts are all vital tools to visually check all reported data values (Locke, 1990).

5. QUALITY ASSURANCE MANAGEMENT PROGRAMME

The process to assure that 'quality' data are reported is an ongoing one. The programme in place at the Dorset Research Centre has been implemented since 1975 as part of the environmental studies carried out by the Limnology Unit of the Ministry of the Environment. The rationale behind a quality assurance programme is to provide a basis for defining and documenting collection, analytical and data creditability in acceptable scientific terms (King, 1982). Quality control activity provides the data upon which quality assurance reports are based. This process implies that preventative measures are implemented in order to prevent error, not to monitor it after it has occurred.

A major part of this programme is the documentation of methodologies, and comparative studies between method types. This report shows that both of these components are an integral part of the studies at the Dorset Research Centre. This documentation process is an on-going one and will continue, as it has in the past, as new projects and studies are developed.

6. QA/QC EVALUATION AND RECOMMENDATIONS

Replicate sampling on the three sites currently monitored now (Clearwater Lake, Dickie 6 and Harp ØF) should continue. These sites cover the widest analytical range in parameters measured at the DRC. Some of these parameters have shown to be beyond acceptable LSB error precision criteria. Intensive QC should continue for precipitation samples, (including containers, samplers and especially the low ionic strength samples). This has proven to be difficult in the past due to low sample volumes. Separate QC precipitation samplers are now in place. Automation of QC data analysis by creating or utilizing computer software to immediately process, update and display QC data will avoid time lags in recognizing problem areas. Finally expansion of the site QC programme to include other agency/site intercomparisons with the DRC site must receive high priority. Several inter-agency data base comparisons are currently in progress. These quality assurance studies will assure credibility and comparability with other data bases.

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8. APPENDICES

Appendix 8.1 Abbreviations used for chemical parameters cited in this report (Locke and Scott, 1986).

Abbreviation	Parameter Description	Reported Units
ACDT	Mineral Acidity	mg/L
ALKT	Total Fixed End Point Alkalinity	"
ALKT3	Total Fixed End Point Alkalinity (pH 3.8)	"
ALKTI	Total Inflection Point Alkalinity (pH 4.5)	"
ALDCV	Catechol-Violet Dialized Aluminum	µg/L
ALNDCV	Catechol-Violet Non-Dialized Aluminum	"
ALDSE	Dialized Aluminum	"
ALNDSE	Non-Dialized Aluminum	"
ALEXCV	Extracted Catechol-Violet Dialized Aluminum	"
ALUT	Total Aluminum	"
CAUR	Calcium	mg/L
CDUT	Cadmium	µg/L
CHLRBT	Chlorophyll b	"
CHLRAT	Chlorophyll a	"
CHLRAC	Chlorophyll a, corrected	"
CLIDUR	Chloride	mg/L
COLAP	Apparent Colour	Hazen Units
COLTR	True Colour	True Colour Units
COND	Conductivity at 25°C	µmhos/cm
CUUT	Copper	mg/L
DO	Dissolved Oxygen	"
DOC	Dissolved Organic Carbon	"
DIC	Dissolved Inorganic Carbon	"
FEUT	Iron	"
FFIDUR	Fluoride	µg/L
KKUR	Potassium	mg/L
MGUR	Magnesium	"
MNUT	Manganese	"
NAUR	Sodium	"
NIUT	Nickel	"
NNHTFR	Ammonium as N	µg/L
NNOTFR	Nitrate and Nitrite as N	"
NNTKUR	Total Kjeldahl Nitrogen (TKN)	"
PBUT	Lead	"
pF	Free Fluoride	dimensionless
pH	pH	"
PPUT	Total Phosphorus	µg/L
SSIO3UR	Silicates as $Si0_2$	mg/L
SSO4UR	Sulphate as SO_4	"
ZNUT	Zinc	µg/L

Appendix 8.2 Quality control replicate chemistry data range summary by parameter by lake strata. The lake data means are from the DRC data base as averages for all study lakes from 76/01 to 86/06. Precision statistics (mean, standard deviation and coefficient of variation) for replicate chemical samples collected from study lakes are available for reference.

Lake abbreviations used in this report:

BC	Blue Chalk	HP	Harp	PC	Plastic
CB	Chub	HY	Heney	RCE	Red Chalk East
CN	Crosson	LI	Lohi	RCM	Red Chalk Main
CR	Clearwater	ME	Middle		

LAKES	Epilimnion			Metalimnion			Hypolimnion		
Parameter	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean
ALKT	5.82	2.06	4.08	8.46	2.04	4.70	13.8	2.02	5.78
ALKTI	3.61	0.29	1.74	5.92	0.24	2.43	11.5	0.19	3.55
ALEXCV	8.60	2.00	3.171						
COND25	34.4	22.6	28.1	35.0	23.6	29.4	42.1	25.6	31.1
pH	6.75	5.76	6.22	6.61	5.48	5.97	6.32	5.45	5.86
FFIDUR	50.2	34.6	38.35	51.3	28.9	37.04	49.9	32.0	37.50
COLTR	36.7	4.81	17.98	66.6	7.72	27.68	94.40	13.0	45.63
NNHTFR	12.3	4.88	7.93	107.	5.38	33.00	425.	2.0	104.8
NNOTFR	37.5	9.87	21.70	119.	12.5	53.43	160.	22.7	88.0
NNTKUR	287.	171.	222.	359.	184.	252.	695.	180.	331.
DIC	0.96	0.30	0.60	2.78	0.60	1.49	5.40	0.60	2.34
PPUT	11.2	4.60	6.93	15.7	6.59	9.82	19.4	5.17	13.1
ALUT	155.	11.0	32.20	100.2	13.5	51.07	106.5	18.2	60.9
FEUT	134.	34.8	75.1	815.	53.8	294.	3090.	50.0	808.6
MNUT	43.3	12.5	26.16	130.	21.4	56.7	6290.	35.0	774.
CAUR	3.05	1.96	2.46	3.10	1.93	2.53	3.59	2.02	2.63
MGUR	0.91	0.45	0.67	0.93	0.46	0.70	1.01	0.47	0.73
NAUR	1.01	0.46	0.70	0.98	0.46	0.71	0.98	0.48	0.71
KKUR	0.53	0.22	0.39	0.54	0.24	0.42	0.54	0.27	0.41
CLIDUR	0.83	0.34	0.50	0.82	0.36	0.51	0.84	0.38	0.52
SSO4UR	8.53	6.76	7.54	8.45	6.40	7.39	8.45	6.02	7.16
SIO3UR	1.08	0.20	0.62	1.50	0.24	0.98	2.25	0.63	1.33
DOC	5.18	1.90	3.43	5.46	1.75	3.35	5.83	1.73	3.44
ZNUT	7.67	2.17	4.34	8.67	3.0	5.71	7.83	4.80	6.04
* ALKT3	8.87	7.16	7.93						
* ALNDCV	168.0	103.0	137.7						
* CDUT	0.443	0.239	0.37						
* PBUT at detection limits			0.001						
* CUUT	0.046	0.040	0.043						
* NIUT	0.198	0.174	0.187						

* whole lake samples only

Appendix 8.3 Stream sample type QC chemistry data summary by parameter. Stream data means are calculated from the QC data results from 1984-87. Precision statistics (mean, standard deviation and coefficient of variation) for replicate chemical samples collected from study streams are available for reference.

Steam abbreviations used in this report:

BC 1	Blue Chalk 1	DE 11	Dickie 11	PC 1	Plastic 1
BC OF	Blue Chalk Outflow	DE OF	Dickie Outflow	PC OF	Plastic Outflow
CB 1	Chub 1	HP 3	Harp 3	RC 1	Red Chalk 1
CB 2	Chub 2	HP 3A	Harp 3A	RC 2	Red Chalk 2
CB OF	Chub Outflow	HP 4	Harp 4	RC 3	Red Chalk 3
CN 1	Crosson 1	HP 5	Harp 5	RC 4	Red Chalk 4
CN OF	Crosson Outflow	HP 6	Harp 6	RC OF	Red Chalk Outflow
DE 5	Dickie 5	HP 6A	Harp 6A	BE 1	Beech 1
DE 6	Dickie 6	HP OF	Harp Outflow	PT 1	Paint 1
DE 8	Dickie 8	HY OF	Heney Outflow	TWS	Twelve Mile South
DE 10	Dickie 10	HY OFA	Heney Outflow A	TWN	Twelve Mile North

STREAMS Parameter	Detection Limits (if not 0.0)	Minimum	Maximum	Mean	N
ACDT		-	-	-	0
ALKT		0.0	80.744	7.949	60
ALKT3		6.734	13.324	10.411	20
ALKTI		-5.434	77.938	4.690	71
ALDCV		-	-	-	0
ALNDCV		6.60	172.60	69.186	21
ALDSE		1.00	19.20	8.125	8
ALNDSE		3.200	169.60	63.200	8
ALEXCV		6.00	151.80	63.219	21
COND25		16.80	146.0	38.467	81
pH		4.034	7.596	5.616	71
FFIDUR		68.94	92.40	45.815	86
COLTR		3.40	580.0	126.25	81
NNHTFR	4.0	4.0	235.0	28.119	77
NNOTFR	2.0	2.0	1160.0	62.504	57
NNTKUR		101.4	1134.0	403.011	35
DIC		0.748	3.793	2.050	21
ALUT		6.80	244.40	96.481	33
PPUT		5.11	149.60	38.097	21
DO		0.52	13.32	8.399	55
CAUR		0.937	23.256	3.811	86
MGUR		0.22	3.79	0.890	66
NAUR		0.280	1.726	0.897	66
KKUR		0.064	1.59	0.413	66
CLIDUR		0.222	2.872	0.867	66
SSO4UR		0.258	15.412	6.561	66
SIO3UR		0.120	4.758	2.028	66
DOC		1.820	38.7	13.387	66
FEUT		0.025	3.66	0.596	86
MNUT	0.005	0.0054	0.456	0.059	66
CDUT	0.001	0.001	0.118	0.060	12
PBUT	0.05	0.05	1.456	0.753	12
ZNUT	0.50	0.50	17.20	8.187	20
pF		5.042	5.539	5.279	8

Appendix 8.4 Precipitation sample type QC chemistry data summary by parameter. The precipitation data means are from the DRC data base as averages for all study sites from 76/01 to 86/06. Defection limits are given in OME, 1986. Precision statistics (mean, standard deviation and coefficient of variation) for replicate chemical samples collected from study precipitation sites are available for reference.

Precipitation site abbreviations used in this report:

PT1P	Paint Lake site	HPP2	Harp Lake site #2
PCP	Plastic Lake site #1	HYP	Heney Lake site #1
PCP2	Plastic Lake site #2	HYP2	Heney Lake site #2
HPP	Harp Lake site #1		

PRECIPITATION

Parameter	Maximum	Minimum	Mean
ACDT	6.804	3.084	4.632
ALKT	0.0	0.314	0.052
ALKTI	-8.773	-1.366	-3.531
ALUT	2.400	30.400	13.356
COND25	21.050	84.899	34.492
pH	3.776	4.584	4.217
PPUT	no replicate data collected in this study		
FFIDUR	0.400	18.580	4.87
NNHTFR	58.2	754.0	274.34
NNTKUR	130.0	1075.0	465.66
NNTKUR	106.0	670.0	240.125
DOC	0.50	1.20	0.73
CAUR	0.012	0.642	0.186
MGUR	0.005	0.156	0.037
NAUR	0.012	0.135	0.061
KKUR	0.01	0.105	0.041
CLIDUR	0.016	0.246	0.139
SSO4UR	0.60	4.42	2.257
SIO3UR	0.010	0.020	0.015
FEUT	0.0125	0.025	0.0187
ZNUT	2.400	67.399	14.115

Appendix 8.5

Graphs of selected parameters illustrating analytical precision of QC replicate samples taken by the Limnology Unit at the Dorset Research Centre (1983-1987). Refer to Appendix 8.1 for standard abbreviations used for chemical parameters.

Not all parameters are presented for each type of graphs. Some of the plots showed no apparent trends or there were not enough values to properly display. For many parameters, the full range of mean standard deviation and mean coefficient of variation were less than the W.Q. published guidelines. Some parameters (trace metals such as NIUT, CVVT, CDUT, PBUT and ZNUT, Aluminum species and ALKT3) do not have any reported W.Q. precision estimates to compare with our QC data. For many trace metals however, measured data was reported at or below detection limits. Those values that were measured showed significantly large variation and are not included in the figures in this appendix.

No data editing has been applied to these data. Outliers do exist as evidenced by some figures. The fact that any outliers are present, and their magnitude, might account for the generally higher precision estimates (std and cov) found in this study. The W.Q. precision figures are produced under laboratory conditions and will not include the broad base of introduced variation that this study encompasses.

8.5.1 Precision by Parameter Analytical Range (Figures 8.1 to 8.19)

These graphs illustrate the mean standard deviation (std) and the mean coefficient of variation (cov) for different sample types is plotted against the analytical range for several parameters measured. The Water Quality (W.Q.) precision estimates (O.M.E., 1986) are given for each range in Table 8.1 The parameters plotted have data replicate precision greater than W.Q. published limits. These figures identify which range of analytical values exceed those limits, and by what factor.

8.5.2 Precision by Study Site for Lake, Stream and Precipitation Samples (Lakes - Figures 8.20 to 8.37, Streams - Figures 8.38 to 8.45, Precipitation - Figures 8.46 to 8.51).

The mean standard deviation (std) and the mean coefficient of variation (cov) for three different sample types is plotted for several parameters. The lake sample QC replicate precision has been further grouped according to the strata sampled (whole lake, epilimnion (epi), metalimnion (meta) and hypolimnion (hypo)). The normal range of values for each parameter for each study site is summarized in Table 8.2. Table 8.3 describes which parameters exceed the W.Q. reported precision grouped by sample type over a broad reported range. Some of the parameters shown do not exceed allowable limits and are presented here to show uniformity of precision over all sites (e.g. precipitation pH, stream pH, DO). These figures identify individual study site(s) (or sample layers) that show QC data precision greater than W.Q. published limits, (Table 8.1).

Other parameters may show individual site variation greater than allowable limits. These values are often hidden after calculating site group mean standard deviations and mean coefficient of variation (e.g. lake site vs. lake strata COND25, stream COND25, DO, DOC). These individual variations may assist in identifying sampling problems unique to each site.

8.5.3 QC Data Statistics Graphs (Lakes - Figures 8.52 to 8.64, Streams - Figures 8.65 to 8.71, Precipitation - Figures 8.72 to 8.77)

The mean standard deviation (std) and mean coefficient of variation (cov) are plotted against the mean for selected parameters replicated for each category of sampling sites. These figures illustrate what, if any, relationship exists between these two estimates of precision and the mean. Parameters such as pH show uniformly low variation across all values measured. Other parameters such as COLTR, ALUT, NNOTFR and SSO4UR show increased std at the high range of values and conversely high cov at the low range. Some graphs show the results of outliers in the data which seem to occur at either the low or high range (MGUR, NAUR, KKUR). The fact that such outliers exist, and the degree of variation from the mean of the other replicates, would suggest field contamination rather than analytical replicability.

8.5.4 QC Data Statistics Time Trends

Three of the study sites, (DE6 - Figures 8.78 to 8.85, HP0 - Figures 8.86 to 8.96 and CR - Figures 8.97 to 8.106) have been replicate sampled from 1984 to present, (see Section 3.1). The mean standard deviation (std) and mean coefficient of variation (cov) for selected parameters are plotted over time. Two of these sites are streams, and certain parameters showed marked seasonal patterns due to fluctuating chemistry. This fact may account for some noted variation in standard deviation and coefficient of variation. Appendices 8.2 and 8.3 give the actual precision statistics for the three sites and clearly shows some seasonal variation in the mean of the replicates. Upward trends in standard deviation apparent for several parameters for some of the sites. No parameter variation however is uniformly increasing or decreasing for all sites.